Journal of CO_2 Utilization 21 (2017) 513–520

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Fabrication of anthocyanin-sensitized nanocrystalline titanium dioxide solar cells using supercritical carbon dioxide

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ARTICLE INFO

Keywords:
Black rice
Dyeing
Supercritical fluid
Anthocyanins
Titanium dioxide
Dye-sensitized
DSSCs

ABSTRACT

This study describes an inexpensive, facile process for fabricating dye-sensitized solar cell (DSSC) using nanocrystalline titanium dioxide as the photoelectrode. The results of this work showed that the low surface tension characteristics of supercritical carbon dioxide could save dyeing time when used as a medium to dye nanocrystalline titanium dioxide photoelectrodes with anthocyanin. Metallographic microscopy observations of the dyed photoelectrodes revealed that the supercritical dyeing process produced a deeper color in the TiO_2 photoelectrode than did dip dyeing. The absorption spectrum of the product showed that the supercritical dyeing time can be shortened to 1/10 that of the traditional dip process under total absorption equivalent. In addition, the I–V characteristics of the dyed photoelectrode exhibited a critical surplus of current and voltage, which was another indication of the superiority of the supercritical dyeing process. The supercritical dye-sensitized photoelectrodes showed improved values of I_{sc} (1.2 mA) and V_{oc} (290 mV).

1. Introduction

Renewable energy is theoretically inexhaustible, with endless resources such as wind, biomass, solar, wave and tidal energy, hydropower and geothermal energy, etc. Broadly speaking, perfecting green energy will increase energy efficiency, reduce greenhouse gas emissions, reduce waste and pollution, and will help save water and other natural resources. To this end, the development of solar renewable energy offers many advantages over conventional energy sources, which has made it very attractive to researchers. [1,2]

The first solar cell was designed in 1839 in France by Alexandre Edmond Becquerel, who found that when the surface of metal electrodes coated with copper oxide or silver halide were exposed to the sun, they produced an electrical voltage. The first exhibition of the PV (photovoltaic) effect was demonstrated at the Bell Laboratories in the United States in 1954 when Chapin et al. demonstrated a photoelectric conversion efficiency of 6% in the first generation of solar cells. Later, in 1988, M. Graetzel developed a low-cost, dye-sensitized solar cell (DSSC) that increased the photoelectric conversion efficiency to 7.1–7.9%. This demonstration of improved efficiency showed that the dye-sensitized solar cell had increased the possibilities for commercial applications of solar cells.

In 2006, Hao et al. [3] used ethanol under controlled temperature conditions to successfully extract natural pigments from black rice, various flowers and seaweed. The authors analyzed the resulting dyes and found that the main chemical in all three source materials was anthocyanin. Anthocyanin-sensitized TiO_2 solar cells had open circuit voltage (V_{oc}) of 550 mV and short circuit current (I_{sc}) of up to 1.14 mA. In 2007, Wongcharee et al. [4] demonstrated an open circuit voltage of 372–404 mV, and a short circuit current of 0.37–1.63 mA for a DSSC fabricated using dyes obtained from rosella and blue pea flowers in a 1:1 mixed volume ratio. Warta et al. [5] also reported the solar cell efficiencies of a number of DSSCs.

It is well known that gases and liquids can become supercritical fluids when they are compressed and heated above their critical pressure and temperature. In this state these supercritical fluids can exhibit properties that are intermediate between those of typical gases and liquids. Compared with liquids, the density and viscosity of supercritical fluids are lower, but diffusion in these materials is greater. Hence, supercritical fluids are widely used in chemical extraction, reactions, polymerization, chromatography, and impregnation of desired additives into various materials. [6–11] In this study, supercritical CO_2 was used as a medium to impregnate a selected dye into TiO_2 photoelectrodes. Supercritical CO_2 fluid was used because it was believed that its lower surface tension characteristics could decrease the time required to dye nanocrystalline titanium dioxide photo-electrodes with anthocyanin.

2. Experimental

The experimental procedure used in this study is summarized in Fig. 1:

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http://dx.doi.org/10.1016/j.jcou.2017.07.006
Received 1 December 2016; Received in revised form 25 June 2017; Accepted 4 July 2017
Available online 05 September 2017

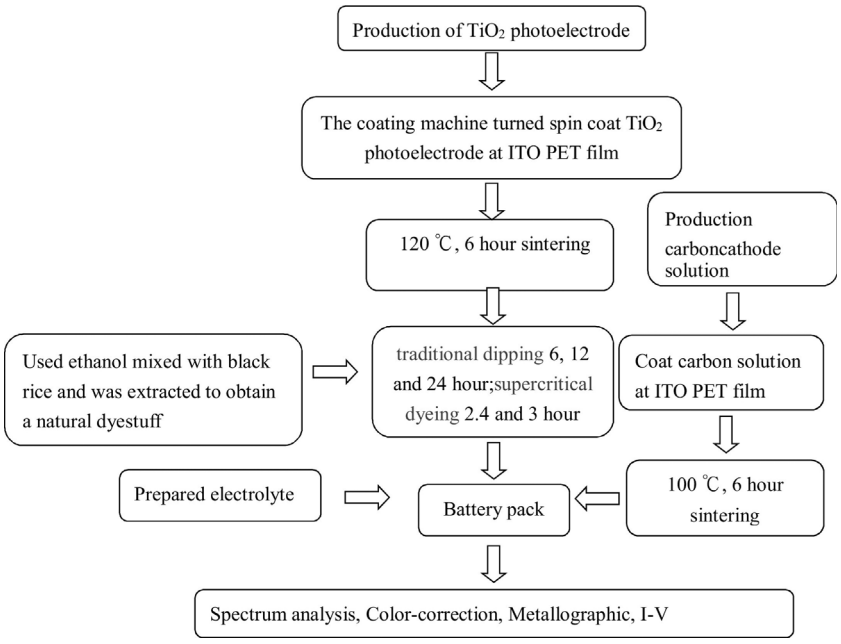

Fig. 1. Experimental Procedure.

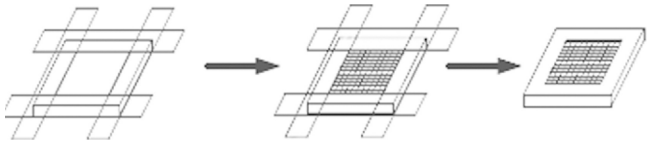

Fig. 2. Steps used to produce the of TiO_2 photoelectrode.

2.1. Production of TiO_2 photoelectrode [12]

First, the film was cut into 3 cm × 3 cm pieces and tapes were pasted on all four sides of the pieces to control the coating area as 2 cm × 2 cm, as shown in Fig. 2. The sizing reagent used to coat the film included 3 g of TiO_2, 6 mL of ethanol, 3 mL of distilled water, and 0.1 mL of acetyl acetone, which was stirred synchronously for 15 min in a sealed container. The taped film was placed on a spin coating machine and was spun at 1000 rpm for 10 s for the first layer of the sizing coating, and then spun at 4000 rpm for 20 s to form the second layer of the coating. The final coating was sintered at 120 ˚C about 6 h.

2.2. Dyeing of TiO_2 photoelectrode

To extract the anthocyanin from black rice, 25 mL of ethanol was mixed with 12 g of black rice and was ball milled for about 5 h using a ball grinder. [4,13,14] The final ground mixture was then centrifuged at 4400 rpm for 90 min and the dye was collected in the supernatant. 20 mL of anthocyanin dye solution was placed in another 25-mL vessel. This vessel was sealed and then purged with gaseous CO_2 into a 200-mL dye pot, which was compressed without circulation, as shown in Fig. 3. [7] The apparatus used for the dyeing procedure was manufactured by Zaar Technical Company. The dyeing apparatus can be compressed to 400 bar and heated to 200 ˚C. In the dyeing procedure used in this study, the pressure was 150 bar and the temperature was 40 ˚C. A series of dyeing procedures was conducted at constant temperature and pressure for 10 min, 2.4 h, and 3.0 h; then, the pressure was released stepwise. At each of these pressure reduction steps, 25 bar of pressure was released, but the temperature was maintained at 40 ˚C for 2 min until the pressure of the vessel was equal to atmosphere pressure. Compared to the supercritical dyeing procedure, the traditional process of dipping the photoelectrode usually requires between 10 min, to 24 h of incubation of the photoelectrode in the dye solution.

2.3. Fabrication of the electrode

The cathode side of the test PV cell was composed of carbon black (0.8 g), graphite (3.2 g), TiO_2 (0.4 g), and 0.8 g of an Sb-SnO_2 mixture (weight ratio = 1:9), all of which were added to 24 mL of 3-methoxy propylnitrile (MPN) and the mixture was magnetically stirred for 10 min in a sealed container. The first layer of the coating of this cathode solution was spun onto the substrate at a spin rate of 1000 rpm for 10 s. The second coat was applied at a speed of 4000 rpm for 20 s.

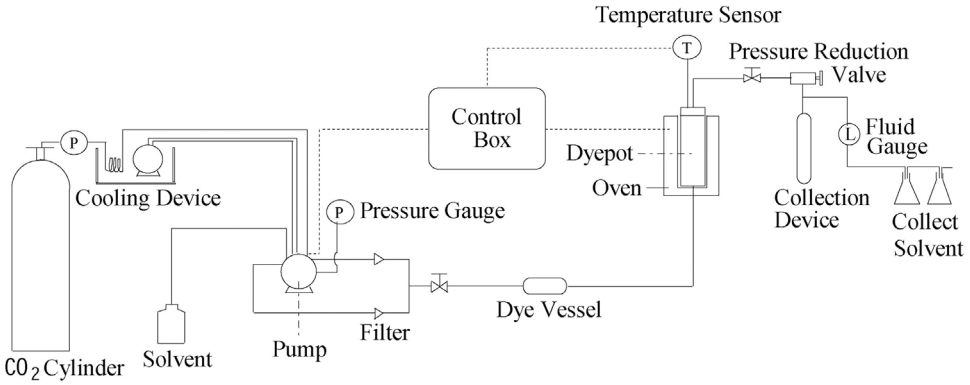

Fig. 3. Schematic diagram of supercritical fluid dyeing system [8].